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New Monocyclopentadienyl Complexes of Titanium(IV) and Zirconium(IV) with Chelating Pyrimidinethiolate, Oxypyrimidine, and Oxypyridine Ligands. Molecular Structure of $[Zr(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}O,N\text{-}ON_2C_6H_7)_3]$[†]

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New monocyclopentadienyl species of Ti(IV) and Zr(IV), namely Cp*MX(SR)$_2$, X = Cl, M = Zr **2**, X = Ph, M = Zr **5**, X = Me, M = Ti **6**, bearing the pyrimidinethiolate ligand, SR, were prepared. In addition, tris-oxipyridine and -oxipyrimidine-containing zirconium complexes, Cp*Zr(OR)$_3$ **9** and **10**, were also isolated. The dynamic behavior of some of them was studied by variable-temperature ^{1}H NMR spectroscopy. The molecular structure of **10** was also established by means of a X-ray diffraction study.

Introduction

In recent years there has been a major effort aimed at investigating the chemistry of group 4 and 5 transition metals with chalcogenide ligands. This interest is due to the important role that such compounds are believed to play as intermediates in different reactions such as desulfurization of organosulfur compounds[1,2] and metal-catalyzed synthetic reactions involving C−S bond cleavage and formation,[3] and in this way, a number of early transition metal thiolate complexes have been prepared.[4]

Continued interest in complexes that incorporate pyridinethiolate and pyrimidinethiolate is caused by several desirable characteristics. Among these is their ability to chelate and bridge transition metals, allowing access to both mono- and oligonuclear products. In addition, they contain functional groups common in crude oils (thiolate-S and aromatic-N), and the pyrimidine group is a constituent of nucleic acids.

In this area, we have recently described[5] the preparation of a family of neutral and cationic pyrimidinethiolate metallocene complexes. The chelating coordination mode and reactivity observed encouraged us to prepare analogous monocyclopentadienyl complexes of group 4 metals. The reported examples of this kind of thiolate compound are very scarce;[4] in fact, the first synthesis of a monocyclopentadienyl zirconium thiolate was published in 1995.[6]

This paper will focus on the synthesis and structural details of new monocyclopentadienyl complexes of titanium(IV) and zirconium(IV) bearing chelating pyrimidinethiolate ligands and analogous oxygen derivatives, oxypyridine and oxypyrimidine ligands.

Results and Discussion

Lithium thiolates have been shown to react with early transition metal chlorides to give metal thiolates in good yields.[7] This methodology has been useful in the synthesis of monocyclopentadienyl-containing bis-thiolate zirconium complexes, such as Cp*ZrCl(SR)$_2$ (Cp* = η^5-C$_5$Me$_5$; SR = C$_6$H$_7$N$_2$S). In fact, the reaction of 1 equiv of Cp*ZrCl$_3$ (**1**) with 2 equiv of the appropriate lithium thiolate in THF at room temperature affords the mono-

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[†] Dedicated to Dr. J. Elguero on the occasion of his 65th birthday.

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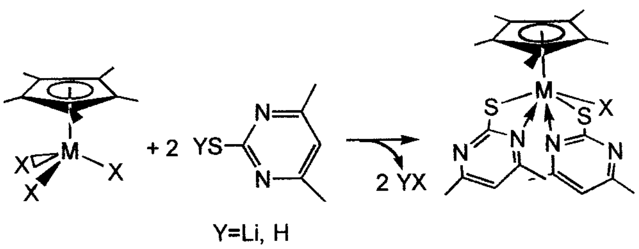
Scheme 1



X=Cl, M=Zr, **1**
X=Ph, M=Zr, **3**
X=Me, M=Ti, **4**

X=Cl, M=Zr, **2**
X=Ph, M=Zr, **5**
X=Me, M=Ti, **6**

cyclopentadienyl bis-thiolate zirconium complex **2** in 63% yield (Scheme 1).

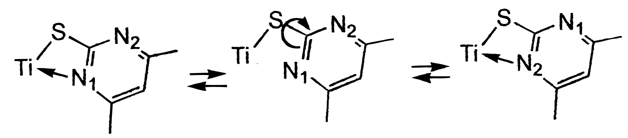
No isolable product was obtained from the reaction between Cp*ZrCl$_3$ and the lithium thiolate in a 1:1 molar ratio. Furthermore, reaction between Cp*ZrCl$_3$ and LiSR in a 1:3 molar ratio affords the bis-thiolate complex **2**.

Complex **2** was isolated as an air-sensitive yellow solid that is insoluble in alkanes but soluble in toluene and THF. Complex **2** was characterized by ^{1}H and ^{13}C NMR and IR spectroscopy. Their room-temperature ^{1}H NMR and ^{13}C{^{1}H} NMR (C$_6$D$_6$) spectra indicate that both thiolate groups are inequivalent and fixed in a rigid disposition where they act as bidentate ligands at this temperature (see Experimental Section).

Furthermore, it has been extensively described that early transition metal alkyl complexes react with acidic reagents, such as alcohols or mercaptans, to yield the corresponding alkane and the alkoxide or thiolate complexes, respectively. It has also been pointed out that the probable mechanism for the protonolysis of the carbon−metal bonds in these processes requires the initial donation of an oxygen or sulfur lone pair of electrons to the metal center.[7] This methodology has proven useful for the synthesis of monocyclopentadienyl-containing alkanethiolate titanium and zirconium compounds such as Cp*M(R)(SR)$_2$. In this way, the reaction of 4,6-dimethyl-2-mercaptopyrimidine with Cp*ZrPh$_3$ (**3**) or with Cp*TiMe$_3$ (**4**) in a 2:1 molar ratio at room temperature affords complexes **5** and **6**, respectively, as shown in Scheme 1.

The same reaction between 4,6-dimethyl-2-mercaptopyrimidine and **3** or **4** in a 1:1 molar ratio gives an intractable mixture of products, which was not characterized. In addition, the reactions in a 3:1 molar ratio afford complexes **5** and **6**.

Scheme 2



Scheme 3

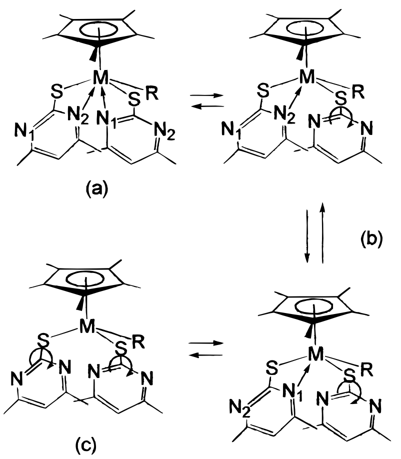


Table 1. Estimated $\Delta G_c^{\#}$ Values for Fluxional Processes in Complex 6

T_c (K)	$\delta\nu$ (Hz)	$\Delta G_c^{\#}$ (kcal·mol^{-1})
335	106.2	16.0(1)
305	21.1	15.5(2)
219	229.6	9.9(2)

Complex **5** was isolated as a white air-sensitive solid, which is virtually insoluble in pentane and partially soluble in toluene and THF. The ^{1}H and ^{13}C NMR spectra of complex **5** at room temperature are very similar to those of complex **2** (see Experimental Section). Complex **6** was obtained as a red air-sensitive solid that is soluble in THF and toluene but virtually insoluble in pentane. This compound has also been characterized by ^{1}H and ^{13}C NMR and IR spectroscopy (see Experimental Section). The ^{1}H NMR spectrum (toluene-d_8) at room temperature exhibits two signals at 1.97 and 2.33 ppm, both of which integrate to six protons, and these correspond to the methyl groups of the inequivalent thiolate ligands. These resonances appear as a broad signal and a sharp singlet, respectively, indicating that fluxional behavior may be occurring in the molecule. This behavior is probably due to the interchange of the positions of the nitrogen atoms of the pyrimidine groups in the coordination sphere of the titanium atom by rotation around the S−C bonds (see Scheme 2).

A variable-temperature ^{1}H NMR study was carried out. Scheme 3 shows the different situations that must be considered.

When the ^{1}H NMR spectrum was recorded at 183 K, four different signals corresponding to the methyl groups of the pyrimidine fragments were found, indicating that rotation around the S−C bond was hindered for both thiolate ligands (Scheme 3, situation a). As the temperature increases, rotation around the C−S bonds becomes easier, and at temperatures above 219 K, only three signals are observed for the methyl groups. One signal integrates as six protons, indicating that while one thiolate acts as a bidentate ligand, the other is bonded to the metal center only by the sulfur atom. For temperature values between 304 and 336 K, the spectrum shows only two methyl signals, each of which integrates as six protons, and one of these signals is broad (Scheme 3, situation b). Finally, above 335 K, a single methyl peak was observed, and this corresponds to free rotation of both ligands, which are now equivalent (Scheme 3, situation c). Three different coalescence temperatures at 219, 305, and 335 K were found. These temperatures and the two site exchange equations[8] can be used to estimate the values of $\Delta G^{\#}$ for the different exchange processes (Table 1).

Compound **6** reacts readily, in C$_6$D$_6$ in an NMR tube at room temperature, with 2,6-dimethylphenyl isocya-

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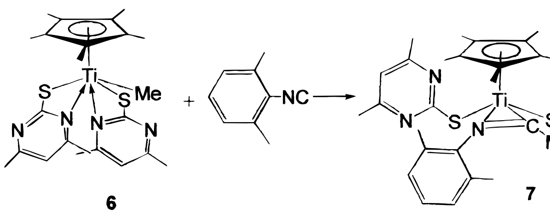
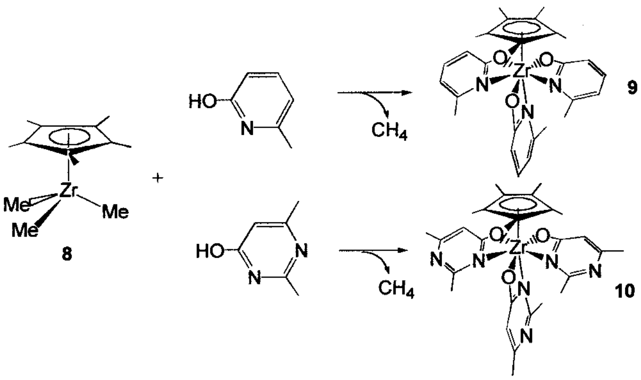
(8) Abrahams, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; John Wiley and Sons: New York, 1988.

Scheme 4



Scheme 5



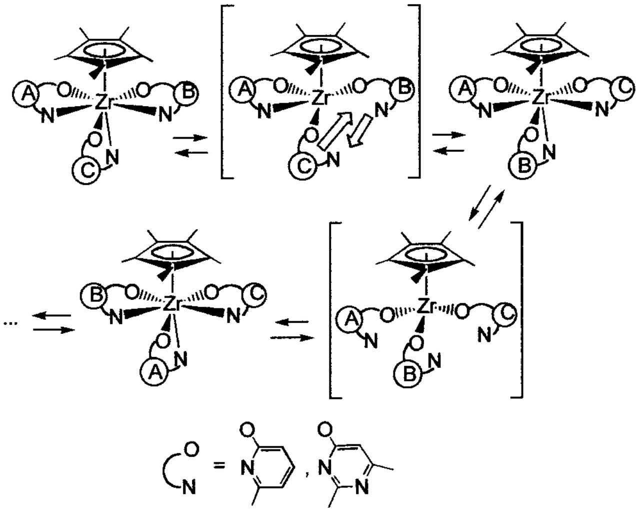
nide in a 1:1 ratio to give the corresponding η^2-iminoacyl complex **7** (Scheme 4) in almost quantitative yield. The complex is extremely air-sensitive, and all attempts to prepare and isolate it on a preparative scale were unsuccessful.

The ^1H and ^{13}C NMR spectroscopic data point to an η^2-coordination of the iminoacyl ligand, while the thiolates act as monodentate ligands. This is in agreement with the situation one would expect based on the literature precedents, which describe early transition metal iminoacyl complexes to be normally stabilized by coordination of the nitrogen atom to the metal center in an η^2-coordination mode.[9] Accordingly, the $^{13}C\{^1H\}$ NMR spectrum shows the signal due to the iminoacyl carbon atom at 226.3 ppm,[10] and the ^1H NMR spectrum shows that the four methyl groups in the pyrimidine moieties are equivalent, which means that free rotation around the C−S bonds occurs (see Experimental Section).

In a similar way, complexes analogous to **2**, **5**, and **6** were obtained when 6-methyl-2-hydroxypyridine (HOpy′) or 2,4-dimethyl-6-hydroxypyrimidine (HOpm′) was reacted (Scheme 5) with Cp*ZrMe$_3$ (**8**) in hexane at room temperature. In these reactions the alkyl groups were completely replaced by the hydroxy groups, even when 1:1 or 2:1 stoichiometries were used.

The complexes Cp*Zr(Opy′)$_3$ (**9**) and Cp*Zr(Opm′)$_3$ (**10**) were isolated as white air-sensitive solids; they are sparingly soluble in alkanes but are soluble in toluene or THF. These compounds have been also characterized by ^1H and ^{13}C NMR and IR spectroscopy (see Experimental Section). Their ^1H NMR spectra at room temperature exhibit broad signals for the pyridine or pyrimidine moieties, indicating that some dynamic process takes place in these molecules. Therefore, the room-temperature ^1H NMR (toluene-d_8) spectrum of compound **9** shows two broad peaks at 1.81 and 2.44 ppm in a 2:1 ratio, and these correspond to the methyl groups of the pyridine moiety (see Experimental Section). A variable-temperature ^1H NMR study was carried out. When the ^1H NMR spectrum was recorded at 193 K, three signals of equal intensity, each integrating as three protons, were observed for the methyl groups of the pyridine moieties, indicating that the three oxypyridine ligands are not equivalent. Different structural situations could be considered, but on the basis of the X-ray crystal structure data obtained for complex **10** (see below) a pentagonal bipyramidal geometry in which the three groups behave as chelate O,N ligands can be proposed (see Scheme 6).

Scheme 6



When the temperature was increased to 223 K two peaks coalesce and two signals were observed, indicating that two groups could exchange their positions around the metal center, probably through a rupture of the metal−nitrogen bonds (see Scheme 6). This exchange gives rise to two equivalent and one inequivalent ligands. At 373 K, a single signal was clearly observed for the methyl groups, and this is in accordance with the fact that the third group would take part in the exchange, giving rise to three equivalent groups (see Scheme 6). A similar dynamic behavior was observed for complex **10**. However, plausible alternative mechanisms for the interchange process that do not involve the breaking of the metal−nitrogen bonds cannot be definitively ruled out.

A single-crystal X-ray analysis of compound **10** was carried out in order to provide precise structural details of this compound and the related complex **9**. The structure of complex **10** is shown in Figure 1 together with the atom-numbering scheme and selected bond lengths and angles.

The Zr atom has a distorted pentagonal bipyramidal geometry, with the Cp* ligand occupying an axial coordination site. The other six sites are occupied by the oxypyrimidine ligands in a chelate fashion. In this way, a nitrogen atom of an oxypyrimidine ligand is almost trans to the Cp* ligand, and the pentagonal base appears to be constituted by the oxygen atom of the same oxypyrimidine ligand and the other two heterocyclic groups.

The pentagonal bipyramidal geometry is distorted. First, the Zr atom is out of the equatorial plane. This can be explained on the basis of an O11−O13 contact

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[9] Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

[10] Martin, A.; Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2117.

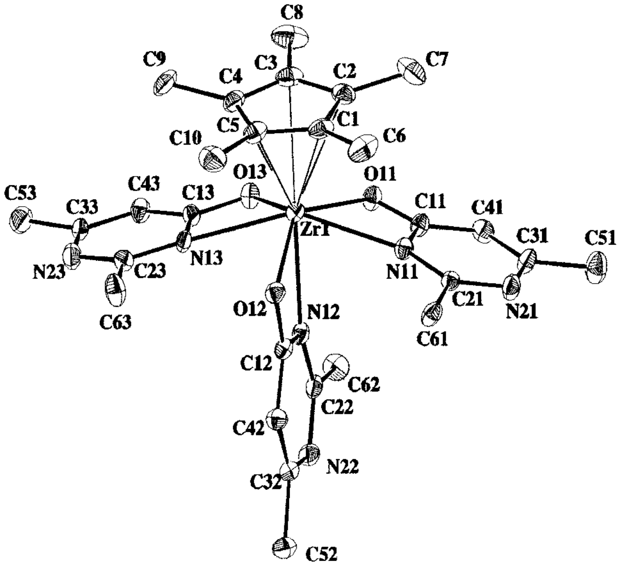

Figure 1. ORTEP drawing of complex **10**, with the atomic labeling scheme. The thermal ellipsoids are at the 30% level of probability. Selected bond distances (Å) and angles (deg), with esd's in parentheses, for complex **10**: Zr(1)−O(11) 2.162(6); Zr(1)−N(12) 2.337(7); Zr(1)−N(11) 2.409(6); O(11)−C(11) 1.288(9); O(11)−Zr(1)−O(13) 73.1(2); N(11)−Zr(1)−N(13) 150.1(2); O(11)−Zr(1)−N(11) 57.7(2); O(11)−C(11)−N(11) 114.3(7).

distance of 2.59 Å (sum of van der Waals radii = 3.04 Å). In addition, there are two other intramolecular contacts between O12 and N13 of 2.91 Å (sum of van der Waals radii = 3.10 Å), and N11 and N12 of 2.83 Å (sum of van der Waals radii = 3.16 Å). These contacts are probably responsible for the deviation of the oxypyrimidine ligand situated in the pseudoaxial position and eliminates the theoretical symmetry plane (Figure 2). This distortion makes the three oxypyrimidine ligands inequivalent around the Zr atom.

Concluding Remarks

In this paper we have reported the synthesis of some new titanium and zirconium monocyclopentadienyl-containing complexes with two or three chelating pyrimidinethiolate, oxypyrimidine, or oxypyridine ligands. These compounds are prepared by halide or alkyl displacement.

Whereas zirconium complexes **2** and **5**, which bear two thiolate ligands, are rigid in solution at room temperature, analogous trisubstituted oxypyridine and oxypyrimidine complexes **9** and **10**, as well as titanium complex **6**, which all bear two thiolate ligands, show a fluxional behavior in solution.

The molecular structure of **10**, as determined by X-ray diffraction studies, shows heptacoordination around the zirconium atom with the three chelate heterocyclic substituents in an asymmetric disposition.

We have also studied the reaction of Cp*Ti(Me)(η^2-$SC_6H_7N_2$)$_3$ (**6**) and 2,6-dimethylphenyl isocyanide, and this process gives rise to the corresponding η^2-iminoacyl complex, as indicated by NMR data.

Experimental Section

General Procedures. All reactions were carried out using Schlenk techniques or a glovebox (model VAC HE-2). Hexane and pentane were distilled from sodium/potassium alloy. All solvents were deoxygenated prior to use.

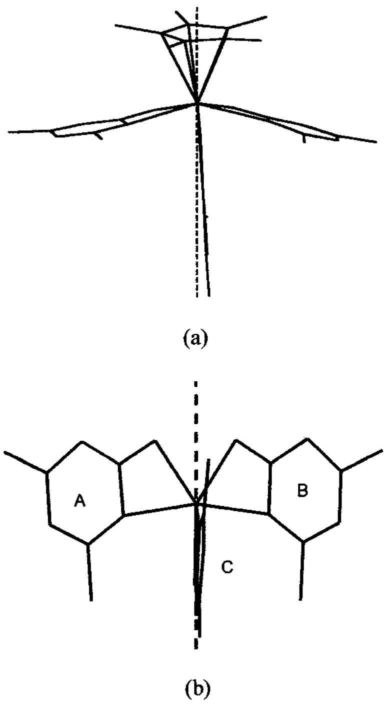

Figure 2. Schematic drawing of complex **10**, indicating the three inequivalent oxypyrimidine ligands, with the theoretical plane of symmetry: (a) front view; (b) top view; the cyclopentadienyl ligand was omitted for clarity.

The following reagents were prepared by literature procedures: Cp*ZrCl$_3$,[11] Cp*ZrMe$_3$,[11] Cp*ZrPh$_3$,[11] Cp*TiCl$_3$,[12] Cp*TiMe$_3$.[13] 2,6-Dimethylphenyl isocyanide was purchased from Fluka, stored over molecular sieves, and deoxygenated before use. Dimethyl-2-mercaptopyrimidine, 2-hydroxy-6-methylpyridine, and 2,4-dimethyl-6-hydroxypyrimidine were used as received from Aldrich.

^{1}H and ^{13}C NMR spectra were obtained on a 300 Unity Varian spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in parts per million relative to SiMe$_4$. IR spectra were obtained in the region 200−4000 cm^{-1} using a Perkin-Elmer 883 spectrophotometer.

Synthesis of Cp*Zr(Cl)(η^2-$SC_6H_7N_2$)$_2$ (2). To a solution of HS($C_6H_7N_2$) (0.22 g, 1.60 mmol) in 5 mL of THF was added 1 mL (1.60 mmol) of ^{n}BuLi (1.6 M hexane solution). The mixture was stirred at room temperature for 30 min. The solution was then cooled at −78 °C, and 0.27 g (0.80 mmol) of Cp*ZrCl$_3$ was added. The mixture was allowed to reach room temperature and stirred for 1 h. The solvent was removed under vacuum, the residue was extracted with toluene, and after filtration, the toluene was evaporated and the yellow oil washed with pentane to afford 0.27 g (63%) of a pale yellow solid, which was characterized as **2**: IR (Nujol/PET, cm^{-1}) 1576 (s), 1529 (s), 1258 (s), 1205 (m), 678 (m), 360 (m), 209 (m); ^{1}H NMR (300 MHz, C_6D_6) δ 1.65 (s, 3H, CH$_3$), 1.89 (s, 3H, CH$_3$), 2.00 (s, 15H, Cp*), 2.01 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$), 5.69 (s, 1H, CH pyrimidine), 5.91 (s, 1H, CH pyrimidine); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 12.6 (Cp*), 20.9 (CH$_3$), 23.6 (CH$_3$), 23.8 (CH$_3$), 24.1 (CH$_3$), 114.9 (CH pyrimidine), 117.0 (CH pyrimidine), 124.8 (Cp*), 161.5 (C−CH$_3$), 165.0 (C−CH$_3$), 168.8 (C−CH$_3$), 169.5 (C−CH$_3$), 175.3 (C−S), 182.5 (C−S). Anal. Calcd

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(11) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

(12) (a) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1156. (b) Hidalgo, G.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37.

for $C_{22}H_{29}N_4ClS_2Zr$: C, 48.90; H, 5.41; N, 10.37. Found: C, 48.87; H, 5.45; N, 10.12.

Synthesis of Cp*Zr(Ph)(η^2-$SC_6H_7N_2$)$_2$ (5). A mixture of Cp*$ZrPh_3$ (0.26 g, 0.57 mmol) and HS($C_6H_7N_2$) (0.16 g, 1.15 mmol) in 20 mL of pentane was stirred at room temperature overnight. The white precipitate was separated by filtration, washed twice with 5 mL of pentane, and vacuum-dried to yield 0.22 g (67%) of **2**: IR (Nujol/PET, cm^{-1}) 1600 (m), 1575 (s), 1525 (s), 1325 (s), 1258 (s), 1016 (m), 691 (m), 433 (m), 350 (s); ^{1}H NMR (300 MHz, C_6D_6) δ 1.82 (s, 3H, CH_3), 1.89 (s, 15H, Cp*), 1.91 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 5.44 (s, 1H, CH pyrimidine), 5.65 (s, 1H, CH pyrimidine), 7.13−7.62 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 12.5 (Cp*), 23.67 (CH_3), 23.71 (CH_3), 23.88 (CH_3), 23.89 (CH_3), 115.1 (CH pyrimidine), 117.2 (CH pyrimidine), 127.0 (Cp*), 123.8, 125.2, 128.5, 135.0 (Ph), 164.5 (C−CH_3), 166.1 (C−CH_3), 168.6 (C−CH_3), 168.8 (C−CH_3), 176.5 (C−S), 180.0 (C−S). Anal. Calcd for $C_{28}H_{34}N_4S_2Zr$: C, 57.79; H, 5.89; N, 9.62. Found: C, 57.82; H, 5.90; N, 9.63.

Synthesis of Cp*Ti(Me)(η^2-$SC_6H_7N_2$)$_2$ (6). A mixture of Cp*$TiMe_3$ (0.86 g, 3.76 mmol) and HS($C_6H_7N_2$) (1.05 g, 7.52 mmol) in 40 mL of toluene was stirred at room temperature for 3 h. After filtration the solvent was evaporated and the red oil was washed with pentane to afford 1.60 g (89%) of a red solid, which was characterized as **3**: IR (Nujol/PET, cm^{-1}) 1620 (m), 1571 (s), 1520 (s), 1260 (s), 1010 (s), 648 (m), 356 (m), 203 (m); ^{1}H NMR (300 MHz, C_6D_6) δ 1.02 (s, 3H, CH_3−Ti), 1.92 (s, 15H, Cp*), 1.97 (s, broad, 6H, CH_3), 2.33 (s, 6H, CH_3), 5.67 (s, 1H, CH pyrimidine), 5.78 (s, 1H, CH pyrimidine); ^{13}C NMR (75 MHz, C_6D_6) δ 13.3 (q, $^1J_{C-H}$ = 126.9 Hz, Cp*), 22.7 (q, $^1J_{C-H}$ = 128.4 Hz, CH_3), 23.4 (q, $^1J_{C-H}$ = 127.4 Hz, CH_3), 24.0 (q, $^1J_{C-H}$ = 127.4 Hz, CH_3), 61.6 (q, $^1J_{C-H}$ = 125.9 Hz, CH_3−Ti), 114.5 (d, $^1J_{C-H}$ = 164.7 Hz, CH pyrimidine), 117.5 (d, $^1J_{C-H}$ = 166.7 Hz, CH pyrimidine), 126.5 (s, Cp*), 163.9 (s, C−CH_3), 166.4 (s, C−CH_3), 167.7 (s, C−CH_3), 178.9 (s, C−S), 181.6 (s, C−S). Anal. Calcd for $C_{23}H_{32}N_4S_2Ti$: C, 57.97; H, 6.77; N, 11.76. Found: C, 57.23; H, 6.92; N, 11.57.

Synthesis of Cp*Ti(η^2-MeCNXylyl)(η^1-$SC_6H_7N_2$)$_2$ (7). A mixture of Cp*Ti(Me)($SC_6H_7N_2$)$_2$ (0.03 g, 0.06 mmol) and 2,6-dimethylphenyl isocyanide (0.01 g, 0.06 mmol) in 0.7 mL of C_6D_6 was allowed to react at room temperature in an NMR tube. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded, and the product was identified as **5**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.54 (s, 3H, CH_3−Ti), 1.95 (s, 15H, Cp*), 2.01 (s, 6H, CH_3), 2.09 (s, 12H, CH_3), 5.93 (s, 2H, CH pyrimidine), 6.52−6.83 (m, 3H, xylyl); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 12.3 (Cp*), 18.6 (CH_3), 19.9 (CH_3), 23.9 (CH_3), 114.1 (CH pyrimidine), 124.9 (Cp*), 126.0, 127.7, 128.5 (CH, xylyl), 132.4 (C−CH_3, xylyl), 144.3 (C−CN, xylyl), 166.4 (C−CH_3, pyrimidine), 179.7 (C−S), 226.3 (C=N).

Synthesis of Cp*Zr(η^2-O,N-ONC_6H_6)$_3$ (9). A mixture of Cp*$ZrMe_3$ (0.25 g, 0.92 mmol) and HO(NC_6H_6) (0.26 g, 2.35 mmol) in 10 mL of hexane was stirred at room temperature for 4 h. The white precipitate was separated by filtration, washed twice with 10 mL of hexane, and vacuum-dried. Recrystallization from dichloromethane/pentane yielded white crystals of **9** (0.40 g, 80%): IR (Nujol/PET, cm^{-1}) 1650 (m), 1617 (m), 1584 (m), 1030 (m); ^{1}H NMR (300 MHz, toluene-d_8) δ 1.81 (s, 3H, CH_3 pyridine), 2.04 (s, 15H, Cp*), 2.44 (s, 6H, CH_3 pyridine), 5.61 (d, 1H, ^3J = 7.00 Hz, CH^{3or5}), 5.95 (d, 2H, ^3J = 7.00 Hz, CH^{3or5}), 6.14 (d, 3H, ^3J = 8.14 Hz, CH^{3or5}), 6.76 (pt, 1H, ^3J = 8.14 Hz, ^3J = 7.00 Hz, CH^4), 6.90 (pt, 2H, ^3J = 8.14 Hz, ^3J = 7.00 Hz, CH^4); $^{13}C\{^1H\}$ NMR (75 MHz, toluene-d_8) δ 11.29 (Cp*), 21.33, 20.43 (CH_3 pyridine), 107.76 (CH^5 pyridine), 110.91, 111.65 (CH^3 pyridine), 121.88 (Cp*), 140.04, 140.31 (CH^4 pyridine), 152.13, 155.05 (C^6 pyridine), 173.55, 173.97 (C^2 pyridine). Anal. Calcd for $C_{28}H_{33}N_3O_3Zr$: C, 61.06; H, 6.04; N, 7.63. Found: C, 61.23; H, 6.18; N, 7.72.

Table 2. Crystal Data and Structure Refinement for Complex 10

empirical formula	$C_{28}H_{36}N_6O_3Zr$
fw	595.85
temperature	293(2) K
wavelength	0.71070 Å
cryst syst, space group	Triclinic, $P\bar{1}$
unit cell dimens	a = 8.868(4) Å, α = 100.11(4)° b = 11.022(6) Å, β = 101.50(3)° c = 16.599(5) Å, γ = 111.20(4)°
volume	1426.8(11) Å^3
Z, calcd density	2, 1.387 g/cm^3
abs coeff	4.25 cm^{-1}
F(000)	620
cryst size	0.4 × 0.3 × 0.2 mm
θ range for data collection	2.06−28.00°
index ranges	$0 \le h \le 11, -14 \le k \le 13, -1 \le l \le 21$
no. of reflns collected/unique	6888/6888
completeness to 2θ = 28.00	100.0%
no. of data/restraints/params	6888/0/344
goodness-of-fit on F^2	1.022
final R indices $[I > 2\sigma(I)]$[a]	R1 = 0.1068, wR2 = 0.2500
extinction coeff	0.005(2)
largest diff peak and hole	1.543 and −2.276 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

Synthesis of Cp*Zr(η^2-O,N-$ON_2C_6H_7$)$_3$ (10). A mixture of Cp*$ZrMe_3$ (0.18 g, 0.92 mmol) and HO($N_2C_6H_7$) (0.22 g, 1.80 mmol) in 10 mL of hexane was stirred at room temperature for 4 h. The white precipitate was separated by filtration, washed twice with 10 mL of hexane, and vacuum-dried. Recrystallization from dichloromethane/pentane afforded 0.32 g of **10** as white crystals (85%): IR (Nujol/PET, cm^{-1}) 1657 (m), 1630 (m), 1551 (m), 1030 (m); ^{1}H NMR (300 MHz, toluene-d_8) δ 1.84 (s, 3H, CH_3 pyrimidine), 1.93 (s, 15H, Cp*), 2.01 (s, 6H, CH_3 pyrimidine), 2.03 (s, 3H, CH_3 pyrimidine), 2.69 (s, 6H, CH_3 pyrimidine), 5.85 (s, 2H, CH pyrimidine), 5.91 (s, 1H, CH pyrimidine); $^{13}C\{^1H\}$ NMR (75 MHz, toluene-d_8) δ 11.11 (Cp*), 22.69, 23.02 (CH_3 pyrimidine), 23.54, 24.19 (CH_3 pyrimidine), 103.28, 103.68 (C5 pyrimidine), 123.07 (Cp*), 162.05, 165.35 (C^4 pyrimidine), 168.18, 169.24 (C^2 pyrimidine), 176.58, 177.69 (C^6 pyrimidine). Anal. Calcd for $C_{28}H_{36}N_6O_3Zr$: C, 56.44; H, 6.09; N, 14.10. Found: C, 56.48; H, 6.31; N, 14.32.

Structure Determination of Complex 10. Crystals of complex **10** that were suitable for X-ray diffraction were obtained by crystallization from toluene/hexane. A prismatic crystal was selected and mounted on a fine glass fiber with epoxy cement. The crystals were of poor quality and diffracted rather weakly; unfortunately, no other crystals could be obtained. Accurate unit-cell parameters were derived from the least-squares fit of the angular setting of 25 high-order reflections. The data collection was perfomed on a Nonius-Mach3 diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.7107 Å) using an $\omega/2\theta$ scan technique to a maximum value of 56°. The compound crystallizes in the triclinic group $P\bar{1}$ with $Z = 2$. The centrosymmetric alternative was initially assumed and later confirmed by computationally stable refinement. There is one molecule of **10** per asymmetric unit. Parameters for the collection and refinement of diffraction data are contained in Table 2. In addition to the usual corrections for Lorentz and polarization effects, a semiempirical correction for absorption correction was applied[14] (maximum and minimum values of the transmission factor were 1.00 and 0.58).

The structure was solved using direct methods[15] and refined first isotropically by full-matrix least-squares using the SHELXL-97[16] program and then anisotropically by blocked

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full-matrix least-squares for all the non-hydrogen atoms. The hydrogen atoms were included in calculated positions and refined "riding" on their parent carbon atoms. The final atomic coordinates for **10** are provided in the Supporting Information.

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Supporting Information Available: For **10**, all crystallographic data (Table SI), final atomic coordinates for the non-hydrogen atoms (Table SII), bond lengths and angles (Table SIII), anisotropic displacement parameters (Table SIV), final atomic coordinates for the hydrogen atoms (Table SV), intermolecular contacts (Table SVI), and possible hydrogen bonds (Table SVII). This material is available free of charge via the Internet at http://pubs.acs.org.

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